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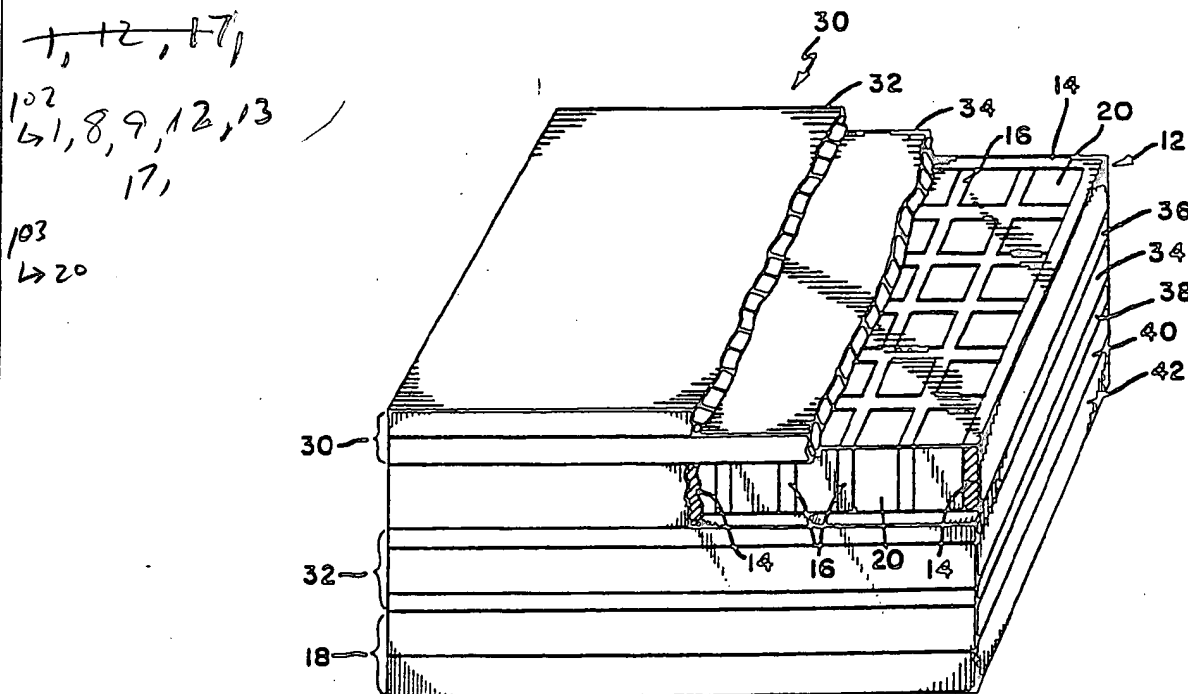
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(54) Title: BALLISTIC RESISTANT COMPOSITE ARMOR



(57) Abstract

A multilayer complex armor having a hard impact layer formed of a plurality of ceramic bodies bound to a surface of a backing layer, a peripheral hard impact layer retaining means positioned about the outer periphery of said hard impact layer, and peripheral ceramic body retaining means positioned about the periphery of each of said ceramic bodies.

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BALLISTIC RESISTANT COMPOSITE ARMORBACKGROUND OF THE INVENTION

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1. Field of the Invention

This invention relates to ballistic resistant composite articles. More particularly, this invention relates to such articles having improved ballistic protection and having improved multiple-hit capability.

10

2. Prior Art

Ballistic articles such as bulletproof vests, helmets, structural members of helicopters and other military equipment, vehicle panels, briefcases, raincoats and umbrellas containing high strength fibers are known. Fibers conventionally used include aramid fibers such as poly (phenylenediamine terephthalamide), graphite fibers, nylon fibers, ceramic fibers, glass fibers and the like. For many applications, such as vests or parts of vests, the fibers are used in a woven or knitted fabric. For many of the applications, the fibers are encapsulated or embedded in a matrix material.

15

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US Patent Nos. 4,623,574 and 4,748,064 disclose a simple composite structure exhibits outstanding ballistic protection as compared to simple composites utilizing rigid matrices, the results of which are disclosed in the patents. Particularly effective are weight polyethylene and polypropylene such as disclosed in US Patent No. 4,413,110.

25

US Patent Nos. 4,737,402 and 4,613,535 disclose complex rigid composite articles having improved impact resistance which comprise a network of high strength fibers such as the ultra-high molecular weight polyethylene and polypropylene disclosed in US Patent No. 4,413,110 embedded in an elastomeric matrix material and at least one additional rigid layer on a major surface of the fibers in the matrix. It is disclosed that the

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composites have improved resistance to environmental hazards, improved impact resistance and are unexpectedly effective as ballistic resistant articles such as armor.

US Patent No. 4,836,084 discloses an armor plate composite composed of four main components, a ceramic impact layer for blunting the tip of a projectile, a sub-layer laminate of metal sheets alternating with fabrics impregnated with a viscoelastic synthetic material for absorbing the kinetic energy of the projectile by plastic deformation and a backing layer consisting of a pack of impregnated fabrics. It is disclosed that the optimum combination of the four main components gives a high degree of protection at a limited weight per unit of surface area.

Ballistic resistant armor made of ceramic tiles connected to a metal substrate exhibit certain properties which substantially reduces the multiple hit capability of the armor. On impact of the projectile, substantial amounts of vibrational energy is produced in addition to the kinetic energy of the impact. This vibrational energy can be transmitted as noise and shock, or can be transmitted to vibration sensitive areas of the armor such as to the ceramic impact layer resulting in a shattering and/or loosening of tiles.

25

SUMMARY OF THE INVENTION

This invention relates to a multilayer complex ballistic armor comprising:

30 (a) a hard impact layer comprised of one or more ceramic bodies bound to a surface of a backing layer;

(b) peripheral hard impact layer retaining means comprising an elastic material positioned about the outer periphery of said hard impact layer and in contact therewith; and

35 (c) peripheral ceramic body retaining means comprising an interconnected network comprising an elastic

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material positioned about the periphery of each of said ceramic bodies comprising said hard impact layer.

Several advantages flow from this invention. For example, through use of the peripheral hard impact layer retaining means and the peripheral ceramic body retaining means, the concentrated impact energy of the projectile can be absorbed without fracture or loss of ceramic bodies surrounding the ceramic body at the point of impact and can be transmitted and distributed throughout the entire complex ballistic armor. Furthermore, through use of this invention the performance of the tiles at the edges of the armor adjacent to peripheral impact layer retaining means and the performance of the portions of individual tiles adjacent to the peripheral ceramic retaining means which is relatively weak are as good as or substantially as good as the performance at the center of the armour and at the center of individual tiles.

BRIEF DESCRIPTION OF THE DRAWINGS

20

The invention will be more fully understood and further advantages will become apparent when reference is made to the following detailed description of the invention and the accompanying drawings in which:

25 FIG 1 is a view in cross-section and in side elevation of an armor plate according to this invention showing its essential elements of a ceramic impact layer, a peripheral hard impact layer retaining means, a peripheral ceramic body retaining means and a backing layer;

30 FIG 2 is a view in cross-section and side elevation of a modified embodiment of this invention depicted in Fig. 2 which includes a cover layer and a release layer.

35 FIG 3 is a view in cross-section and side elevation of a modified embodiment of this invention depicted in FIG 2 which includes vibration isolating layer.

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DETAILED DESCRIPTION OF THE INVENTION

The present invention will be better understood by those of skill in the art by reference to the above
5 figures. Referring to FIG 1, the numeral 10 indicates a ballistic resistant article 10. Article 10, as shown in FIG 1, comprises four main components; a ceramic impact layer 12, peripheral hard impact layer retaining means 14, peripheral ceramic body retaining means 16, and a backing
10 layer 18.

A ceramic impact layer 12 is excellently suitable for blunting the tip of the projectile, particularly because the ceramic material forming layer 12 will retain its hardness and strength despite the high increase in
15 temperature that will occur in the region struck by a projectile. Ceramic impact layer 12 comprises one or more ceramic bodies 20. In the preferred embodiments of the invention, layer 12 comprises a plurality of ceramic bodies 20, in the more preferred embodiments of the
20 invention layer 12 comprises at least about four ceramic bodies 20 and in the most preferred embodiments, layer 12 comprises at least about nine ceramic bodies 20 with those embodiments in which the number of ceramic bodies 20 in layer 12 is at least about sixteen being the embodiment of
25 choice.

Ceramic body 20 is formed of a ceramic material. As used herein, a "ceramic material" is an inorganic material having a hardness of at least about Brihell hardness of 25 or Mohs hardness of 2. Useful ceramic materials may vary
30 widely and include those materials normally used in the fabrication of ceramic armor which function to partially deform the initial impact surface of a projectile or cause the projectile to shatter. Illustrative of such metal and non-metal ceramic materials are those described in C.F.
35 Liable, Ballistic Materials and Penetration Mechanics, Chapters 5-7 (1980) and include single oxides such as aluminum oxide (Al_2O_3), barium oxide (BaO), beryllium oxide (BeO), calcium oxide (CaO) cerium oxides (Ce_2O_3

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and CeO_2), chromium oxide (Cr_2O_3), dysprosium oxide (Dy_2O_3), erbium oxide (Er_2O_3), europium oxides (EuO , Eu_2O_3 , Eu_2O_4 and $\text{Eu}_{16}\text{O}_{21}$), gadolinium oxide (Gd_2O_3), hafnium oxide (HfO_2), holmium oxide (Ho_2O_3), lanthanum oxide (La_2O_3), lutetium oxide (Lu_2O_3), magnesium oxide (MgO), neodymium oxide (Nd_2O_3), niobium oxides (NbO , Nb_2O_3 , NbO_2 and Nb_2O_5), plutonium oxides (PuO , Pu_2O_3 and PuO_2), praseodymium oxides (PrO_2 , Pr_6O_{11} and Pr_2O_3),

10 promethium oxide (Pm_2O_3), samarium oxides (SmO), (Sm_2O_3), scandium oxide (Sc_2O_3), silicon dioxide (SiO_2), strontium oxide (SrO), tantalum oxide (Ta_2O_5), ytterbium oxides (Tb_2O_3 and Tb_4O_7), thorium oxide (ThO_2), thulium oxide (Tm_2O_3),

15 titanium oxides (TiO , Ti_2O_3 , Ti_3O_5 and TiO_2), uranium oxides (UO_2 , U_3O_8 and UO_3), vanadium oxides (VO , V_2O_3 , VO_2 and V_2O_5), ytterbium oxide (Yb_2O_3), yttrium oxide (Y_2O_3), and zirconium oxide (ZrO_2). Useful ceramic materials also include boron

20 carbide, zirconium carbide, beryllium carbide, aluminum beride, aluminum carbide, boron carbide, barium titanate, silicon nitride, calcium titanate, tantalum carbide, graphites, tungsten; the ceramic alloys which include cordierite/MAS, lead zirconate titanate/PLZT,

25 alumina-titanium carbide, alumina-zirconia, zirconia-cordierite/ZrMAS; the fiber reinforced ceramics and ceramic alloys; glassy ceramics; silicon carbide, aluminum carbide, titanium nitride, boron nitride, titanium carbide, titanium diboride, iron carbide,

30 aluminum nitride, iron nitride, barium titanate, titanium niobate, boron carbide, silicon boride, as well as other useful materials. Preferred materials for fabrication of ceramic body 16 in Fig. 2 are aluminum oxide, and metal and non metal nitrides, borides and carbides. The most

35 preferred material for fabrication of ceramic body 18 is aluminum oxide and titanium diboride.

The structure of ceramic body 20 can vary widely depending on the use of the article. For example, ceramic

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body 20 can be a unitary structure composed of one ceramic material or of multilayer construction of the same material or of different ceramic materials.

While in the figures ceramic body 20 is depicted as a
5 cubular solid, the shape of ceramic body 20 can vary widely depending on the use of the article. For example, ceramic body 20 can be an irregularly or a regularly shaped body. Illustrative of a useful ceramic body 20 are
10 cubular, rectangular, cylindrical, and polygonal (such as triangular, pentagonal and hexagonal) shaped bodies. In the most preferred embodiments of this invention, ceramic body 20 is of cubular, rectangular or cylindrical cross-section.

The size (width and height) of ceramic body 20 can
15 also vary widely depending on the use of article 10. For example, in those instances where article 10 is intended for use in the fabrication of light ballistic resistant composites for use against light armaments, ceramic body 20 is generally smaller; conversely where article 10 is
20 intended for use in the fabrication of heavy ballistic resistant composites for use against heavy armaments then ceramic body 20 is generally larger.

The embodiment 10 of FIG 1 includes peripheral ceramic body retaining means 20 between individual ceramic
25 bodies 16 and a peripheral hard impact layer retaining means 14. Peripheral ceramic body retaining means 16 and peripheral hard impact layer retaining means 14 minimizes or reduces the differences in ballistic resistant performance of ceramic impact layer 12 at the edges of
30 ceramic layer 12 and ceramic bodies 20, and at the seams formed by adjacent ceramic bodies 20, which because of the segmented nature of ceramic layer 12 normally tends to be relatively weak areas, and at or about the center of ceramic bodies 20 and ceramic layer 12 which tends to be
35 relatively strong areas. The relative performance of the armor of this invention can be expressed as the efficiency of penetration resistance.

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The specific energy absorption (SEA) is employed to determine the difference in the penetration resistance performance (or the % efficiency of penetration resistance) at the weak areas (such as seams, edge, and corner) as compared to that for the center of tile (strong area). The specific energy absorbed during a ballistic impact is calculated based on the areal density (AD) using the following equation:

$$SEA \text{ (Jm}^2\text{/kg)} = 1/2 [mv^2/AD]$$

where

m is mass of projectile;

V is velocity of projectile which is statistically at the borderline of complete penetration (i.e. the projectile velocity which has a 50% probability of penetrating the target) and AD is the areal density and is the weight of armor per unit area kg/m^2 .

The % efficiency can be calculated using the following equation:

$$\% \text{ efficiency} = 100\% \times [1 - DSEA/SEAc]$$

where

SEAc is the specific energy absorption at about the center of ceramic body 20; and

DSEA is the difference in specific energy absorption and is equal to SEA - specific energy absorption at the weak areas.

In the preferred embodiments of the invention, the % efficiency at about the seam between adjacent ceramic bodies 20 is at least about 80% of the % efficiency at or about the center of at least one of said adjacent ceramic bodies 20, the % efficiency at or about an edge of a ceramic body 20 is at least 70% of the % efficiency at or about the center of said ceramic body 20 and the % efficiency at or about a corner of a ceramic body 20 is at least about 60% of the % efficiency at or about the center

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of said ceramic body 20. In the more preferred embodiments of the invention, the % efficiency at or about a seam between adjacent ceramic bodies 20, at or about an edge of a ceramic body 20 and at or about a corner of a ceramic body 20 is at least about 95% of the % efficiency at or about the center of ceramic body 20, and in the most preferred embodiments of the invention, the % efficiency at or about a seam between adjacent ceramic bodies 20, at or about an edge of ceramic body 20 and at or about a corner of ceramic body 20 is at least about 99% of the efficiency at or about the center of ceramic body 20. Peripheral ceramic body retaining means 16 also allows the maximum loading of ceramic bodies 20 in segmented ceramic impact layer 12, provides optimized spacing between adjacent ceramic bodies 20; retains un-impacted ceramic bodies 20 in place upon severe impact deformation; and transmits and distributes the impact shock to the entire composite upon impact.

Peripheral ceramic body retaining means 16 and hard impact layer retaining means 14 are composed of an "elastic material", which may vary widely and may be metallic, semi-metallic material, an organic material and/or an inorganic material. As used herein an "elastic material" is a material which is herently rigid, capable of free standing without collapsing.

Illustrative of such materials are those described in G.S. Brady and H.R. Clauser, Materials Handbook, 12th edition (1986). Illustrative of the preferred materials for use of backing material described earlier are suitable for use as materials for peripheral ceramic body retaining means 16 and peripheral hard impact layer retaining means 14.

Useful materials include high modulus thermoplastic polymeric materials such as polyamides as for example aramids, nylon 6 and nylon 66, and the like; polyesters such as poly(ethylene terephthalate), poly(butylene terephthalate), and the like; acetalo, polysulfones; polyethersulphones; polyacrylates, acylonitrile/butadine/

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- styrene copolymers, poly(amideimide), poly(etherethar ketones), polycarbonates; polyphenylenesulfides; polysulfides, vinylesters, polyurethanes, polyphenylene oxides; polyestercarbonates; polyesterimides and the like;
- 5 thermosetting resins such as epoxy resins, phenolic resins, saturated polyesters, silicones, polyurethanes, alkyd resins, melamine and urea resins and the like; polymer alloys and blends of thermoplastics polymers and/or thermosetting resins described above; and
- 10 interpenetrating polymer networks such as those of polycyanate ester of a polyol such as the dicyanoester bisphenol and a thermoplastic such as polysulfone. The material may be reinforced by high strength filaments such as aramid filament, Spectra® extended chain polyethylene
- 15 filaments, boron filament, poly glass filaments, ceramic filaments, carbon and graphite filament, and the like.

Useful preferred materials for fabrication of peripheral ceramic body retaining means 16 and peripheral hard impact layer retaining means 14 also include metals

20 such as nickel, manganese, tungsten, magnesium, titanium, aluminum and steel. Useful and preferred steels include carbon steels such as mild steels of grades AISI 1005 to AISI 1030, medium-carbon steels of grades AISI 1030 to AISI 1055, high-carbon steels of the grades AISI 1060 to

25 AISI 1095, free-machining steels, low-temperature carbon steels, rail steel, and superplastic steels; high-speed steels such as tungsten steels, molybdenum steels, chromium steels, vanadium steels, and cobalt steels; hot-die steels; low-alloy steels; low-expansion alloys;

30 mold-steel; nitriding steels such as low-and medium-carbon steels with combinations of chromium and aluminum, or nickel, chromium, and aluminum; silicon steel such as transformer steel and silicon-manganese steel; ultrahigh-strength steels such as medium-carbon low alloy

35 steels, chromium-molybdenum steel, chromium-nickel-molybdenum steel, iron-chromium-molybdenum-cobalt steel, quenched-and-tempered steels, and cold-worked high-carbon steel; stainless steels such as iron-chromium alloy

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austensitic steels, chromium-nickel austensitic stainless steels, and chromium-manganese steel. Useful and preferred materials also include alloys such as manganese alloys, manganese aluminum alloy, manganese bronze alloy; 5 nickel alloys, nickel bronze alloy, nickel cast iron alloy, nickel-chromium alloys, nickel-chromium steel alloy, nickel copper alloy, nickel-molybdenum iron alloy, nickel-molybdenum steel alloy, nickel-silver alloy, nickel-steel alloy; iron-chromium-molybdenum-cobalt steel 10 alloy; magnesium alloys; aluminum alloys such as aluminum alloy 1000 series of commercially pure aluminum, aluminum-manganese alloys of aluminum alloy 300 series, aluminum-magnesium-manganese alloys, aluminum-magnesium alloys, aluminum-copper alloys, aluminum-silicon- 15 magnesium alloys of 6000 series, aluminum-copper-chromium of 7000 series, aluminum casting alloys; aluminum brass alloy, and aluminum bronze.

The ceramic bodies 20 are attached to backing layer 18 which supports hard impact layer 12 peripheral hard 20 impact layer retaining means 14 and peripheral ceramic body retaining means 16, and which provides additional ballistic protection. The amount of a surface of backing layer 18 covered by ceramic bodies 20 may vary widely. In general, the greater the area percent of surface covered 25 or surface loaded, the more effective the protection, and conversely, the lower the area percent of surface covered the less effective the protection. In the preferred embodiments of the invention, the area percent of the surface of backing layer 18 covered by ceramic bodies 20 30 is equal to or greater than about 95 area percent based on the total area of backing layer 18, and in the more preferred embodiments of the invention the area percent covered is equal to or greater than about 97 area percent on the aforementioned basis. Amongst the more preferred 35 embodiments of the invention, most preferred are those embodiments in which the area percent of the surface of backing layer 18 covered by ceramic bodies 20 is equal to

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or greater than about 98 or 99 area percent based on the total surface area of backing layer 18.

Means for attaching ceramic bodies 20 to backing layer 18 may vary widely and may include any means normally used on the art to provide this function. Illustrative of useful attaching means are adhesive such as those described in Liable, Chapter 6, supra, bolts, screws, mechanical interlocks adhesives such as metal and non-metal adhesives, organic adhesives and the like. In the preferred embodiments of this invention attaching means is selected from the group consisting of flexible adhesive bonding agents. Such flexible bonding agents provide several useful functions. For example, such agents enhance structural performance such that the compsite is capable of withstanding severe impact loads, and they enhance the retention of segmented tiles which are not at the point of impact and the retention of spall/particles created by the shattering of tiles on impact. Such adhesive also enhance the conversion of absorbed energy into heat. As used herein, a "flexible adhesive" is a polymeric adhesive which exhibits a Shore A Hardness of from about 15 to 120.

In the preferred embodiments of the invention, the adhesive material is a low modulus, elastomeric material which has a tensile modulus, measured at about 23°C, of less than about 7,000 psi (41,300 kpa). Preferably, the tensile modulus of the elastomeric material is less than about 5,000 psi (34,500 kpa), more preferably is less than 1,000 psi (5900 kpa) and most preferably is less than about 500 psi (3450 kpa) to provide even more improved performance. The glass transition temperature (Tg) of the elastomeric material (as evidenced by a sudden drop in the ductility and elasticity of the material) is less than about 0°C. Preferably, the Tg of the elastomeric material is less than about -40°C, and more preferably is less than about -50°C. The elastomeric material also has an elongation to break of at least about 5%. Preferably, the elongation to break of the elastomeric material is at

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least about 30%. Representative examples of suitable elastomeric materials for use as a flexible adhesive are those which have their structures, properties, and formulation together with cross-linking procedures

5 summarized in the Encyclopedia of Polymer Science, Vol. 5 in the section Elastomers-Synthetic (John Wiley & sons Inc., 1964) and "Handbook of Adhesives", Van Nostrand Reinhold Company (1977), 2nd Ed., Edited by Irving Skeist. Illustrative of such materials are block

10 copolymers of conjugated dienes such as butadiene and isoprene, and vinyl aromatic monomers such as styrene, vinyl toluene and t-butyl styrene; polydienes such as polybutadiene and polychloroprene, polyisoprene; natural rubber; copolymers and polymers of olefins and dienes such

15 as ethylene-propylene copolymers, ethylene-propylene-diene terpolymers and poly(isobutylene-co-isoprene), polysulfide polymers, polyurethane elastomers, chlorosulfonated polyethylene; plasticized polyvinylchloride using dioctyl phthate or other plasticizers well known in the art,

20 butadiene acrylonitrile elastomers, , polyacrylates such as poly(acrylic acid), poly(methylcyanoacrylate), poly(methylacrylate), poly(ethyl acrylate), poly(propylacrylate) and the like; polyacrylics such as poly(acrylonitrile), poly(methylacrylonitrile),

25 poly(acrylamide), poly(N-isopropylacrylamide) and the like, polyesters; polyethers; fluoroelastomers; poly(bismaleimide); flexible epoxies; flexible phenolics; polyurethanes; silicone elastomers; epoxy-polyamides; poly(alkylene oxides); polysulfides; flexible polyamides;

30 unsaturated polyesters; vinyl esters, polyolefins, such as polybutylene and polyethylene; polyvinyls such as poly(vinyl formate), poly(vinylbenzoate), poly(vinyl-carbazole), poly(vinylmethylketone), poly(vinyl-methyl ether), polyvinyl acetate, polyvinyl butyral, and

35 poly(vinyl formal); and polyolefinic elastomers.

Preferred adhesives are polydienes such as polybutadiene, polychloroprene and polyisoprene; olefinic and co-polymers such as ethylene-propylene copolymers,

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ethylene-propylene-diene copolymers, isobutylene-isoprene copolymers, and chlorosulfonated polyethylene; natural rubber; polysulfides; polyurethane elastomers; polyacrylates; polyethers; fluoroelastomer; unsaturated
5 polyesters; vinyl esters; alkyds; flexible epoxy; flexible polyamides; epichlorohydrin; poly vinyls; flexible, phenolics; silicone elastomers; thermoplastic elastomers; copolymers of ethylene, polyvinyl formal, polyvinyl butyal; and poly(bis-maleimide). Blends of any
10 combination of one or more of the above-mentioned adhesive materials. Most preferred adhesives are polybutadiene, polyisoprene, natural rubber, ethylene-propylene copolymers, ethylene-propylene-diene terpolymers, polysulfides, polyurethane elastomers, chlorosulfonated
15 polyethylene, polychloroprene, poly(isobutylene-co-isoprene), polyacrylates, polyesters, polyethers, fluoroelastomers, unsaturated polyesters, vinyl esters, flexible epoxy, flexible nylon, silicone elastomers, copolymers of ethylene, polyvinyl formal, poly vinyl
20 butryal. Blends of any combination of one or more of the above-mentioned adhesive materials.

Backing layer 18 is a rigid layer which functions to support hard ceramic impact layer 12. The term "rigid" is used in the present specification and claims is intended
25 to include structures which are free standing without collapsing which includes semi-flexible and semi-rigid structures. The material employed in backing layer 18 may vary widely, and may be a metallic material, a semi-metallic material, an organic material and/or an
30 inorganic material. Illustrative of such materials are those described in G.S. Brady and H.R. Clauser, Materials Handbook, 12th edition (1986). Backing layer 18 is comprised of a ballistic resistant material which may vary widely depending on the uses of article 10, and offers
35 additional ballistic protection. Backing layer 18 can comprise a single layer or can comprise a plurality of layers of the same material or different materials. In

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the preferred embodiments of this invention, backing layer 18 comprises one or more rigid layers.

Preferred materials used in the fabrication of backing layer 18 are those materials preferred for use in the fabrication of peripheral hard impact layer retaining means 14 and peripheral ceramic body retaining means 16. Such preferred materials include metals such as nickel, manganese, tungsten, magnesium, titanium, aluminum and steel and alloys such as manganese alloys, nickel alloys, and aluminum alloys which make optionally in fibrous reinforcement by inorganic fibers such as silicone carbide. Such materials also include thermoplastic polymeric materials such as polycarbonates; polyether ether, polyamides, polyesters, ketones, polysulfides, polyethersulfones, polyacrylate, acrylonitrile/butadiene/styrene copolymers, poly(amideimide), polyphenylene-sulfides; polyurethanes, polyphenylene oxides, polyesterercarbonates; polyesterimides, and the like; and thermoset resins such as epoxy resins, phenolic resins, vinyl ester resins, modified phenolic resins, unsaturated polyester, allylic resins, alkyd resins, urethanes and melamine and urea resins; polymer alloys and blends of thermoplastics and/or thermosetting resins; and interpenetrating polymer network such as those of polycyanatopolyol such as dicyanoester bisphenol A and a thermoplastic resin such as polysulfone.

In the most preferred embodiments of this invention backing layer 18 comprises one or more layers at least one of which comprises a network of high strength filaments having a tenacity of at least about 7 grams/denier, a tensile modulus of at least about 160 grams/denier and an energy-in-break of at least about 8 joules/gram in a matrix. The fibers in the backing layer 18 may be arranged in networks having various configurations. For example, a plurality of filaments can be grouped together to form a twisted or untwisted yarn bundles in various alignment. In preferred embodiments of the invention, the filaments are aligned substantially parallel and

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unidirectionally to form a uniaxial layer in which a matrix material substantially coats the individual filaments. Two or more of these layers can be used to form a layer 18 with multiple layers of coated

5 unidirectional filaments in which each layer is rotated with respect to its adjacent layers. An example is a with the second, third, fourth and fifth layers rotated $+45^\circ$, -45° , 90° and 0° with respect to the first layer, but not necessarily in that order. Other examples include a layer

10 12 with a $0^\circ/90^\circ$ layout of yarn or filaments.

The type of filaments used in the fabrication of layer 18 may vary widely and can be metallic filaments, semi-metallic filaments, inorganic filaments and/or organic filaments. Preferred filaments for use in the

15 practice of this invention are those having a tenacity equal to or greater than about 10 g/d, a tensile modulus equal to or greater than about 150 g/d, and an energy-in-break equal to or greater than about 8 joules/grams. Particularly preferred filaments are those

20 having a tenacity equal to or greater than about 20 g/d, a tensile modulus equal to or greater than about 500 g/d and energy-to-break equal to or greater than about 30 joules/grams. Amongst these particularly preferred embodiments, most preferred are those embodiments in which

25 the tenacity of the filaments are equal to or greater than about 25 g/d, and energy-to-break is equal to or greater than about 35 joules/gram. In the practice of this invention, filaments of choice have a tenacity equal to or greater than about 30 g/d and the energy-to-break is equal

30 to or greater than about 40 joules/gram.

Illustrative of useful organic filaments are those composed of aramids (aromatic polyamides), such as poly(m-xylylene adipamide), poly(p-xylylene sebacamide), poly 2,2,2-trimethylhexamethylene terephthalamide), poly

35 (piperazine sebacamide), poly (metaphenylene isophthalamide) (Nomex) and poly (p-phenylene terephthalamide) (Kevlar); and aliphatic and cycloaliiphatic polyamides, such as the copolyamide of 30%

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- hexamethylene diammonium isophthalate and 70% hexamethylene diammonium adipate, the copolyamide of up to 30% bis-(-amidocyclohexyl)methylene, terephthalic acid and caprolactam, polyhexamethylene adipamide (nylon 66),
- 5 poly(butyrolactam) (nylon 4), poly (9-aminononanoic acid) (nylon 9), poly(enantholactam) (nylon 7), poly(capryllactam) (nylon 8), polycaprolactam (nylon 6), poly (p-phenylene terephthalamide), polyhexamethylene sebacamide (nylon 6,10), polyaminoundecanamide (nylon 11),
- 10 polydodecanolactam (nylon 12), polyhexamethylene isophthalamide, polyhexamethylene terephthalamide, polycaproamide, poly(nonamethylene azelamide) (nylon 9,9), poly(decamethylene azelamide) (nylon 10,9), poly(decamethylene sebacamide) (nylon 10,10), poly[bis-(4-amino-
- 15 cyclohexyl) methane 1,10- decanedicarboxamide] (Qiana) (trans), or combination thereof; and aliphatic, cycloaliphatic and aromatic polyesters such as poly(1,4-cyclohexylidene dimethyl eneterephthalate) cis and trans, poly(ethylene-1, 5-naphthalate), poly(ethylene-2,6-
- 20 naphthalate), poly(1, 4-cyclohexane dimethylene terephthalate) (trans), poly(decamethylene terephthalate), poly(ethylene terephthalate), poly(ethylene isophthalate), poly(ethylene oxybenzoate), poly(para-hydroxy benzoate), poly(dimethylpropiolactone), poly(decamethylene adipate),
- 25 poly(ethylene succinate) and the like.

- Also illustrative of other useful organic filaments for use in the fabrication of backing layer 18 are those of liquid crystalline polymers such as lyotropic liquid crystalline polymers which include polypeptides such as
- 30 poly γ -benzyl L-glutamate, aromatic polyamides such as poly(1,4-benzamide), poly(chloro-1,4-phenylene terephthalamide), poly(1,4-phenylene fumaramide), poly(chloro-1,4-phenylene fumaramide), poly(4,4'-benzanilide trans, trans-muconamide), poly(1,4-phenylene
- 35 mesaconamide), poly(1,4-phenylene) (trans-1,4-cyclohexylene amide), poly(chloro-1,4-phenylene) (trans-1,4-cyclohexylene amide), poly(1,4-phenylene 1,4-dimethyl-trans-1,4-cyclohexylene amide), poly(1,4-

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- phenylene 2,5-pyridine amide), poly(chloro-1,4-phenylene 2,5-pyridine amide), poly(3,3'-dimethyl-4,4'-biphenylene 2,5 pyridine amide), poly(1,4-phenylene 4,4'-stilbene amide), poly(chloro-1,4-phenylene 4,4'-stilbene amide),
- 5 poly(1,4-phenylene 4,4'-azobenzene amide), poly(4,4'-azobenzene 4,4'-azobenzene amide), poly(1,4-phenylene 4,4'-azoxybenzene amide), poly(4,4'-azobenzene 4,4'-azoxybenzene amide), poly(1,4-cyclohexylene 4,4'-azobenzene amide), poly(4,4'-azobenzene terephthal amide),
- 10 poly(3,8-phenanthridinone terephthal amide), poly(4,4'-biphenylene terephthal amide), poly(4,4'-biphenylene 4,4'-bibenzo amide), poly(1,4-phenylene 4,4'-bibenzo amide), poly(1,4-phenylene 4,4'-terephthylene amide), poly(1,4-phenylene 2,6-naphthal amide), poly(1,5-
- 15 naphthylene terephthal amide), poly(3,3'-dimethyl-4,4'-biphenylene terephthal amide), poly(3,3'-dimethoxy-4,4'-biphenylene terephthal amide), poly(3,3'-dimethoxy-4,4'-biphenylene 4,4'-bibenzo amide), polyoxamides such as those derived from 2,2'-dimethyl-4,4'-diamino biphenyl and
- 20 chloro-1,4-phenylene diamine; polyhydrazides such as poly chloroterephthalic hydrazide and those derived from oxalic, terephthalic, chloroterephthalic, and 2,5-pyridine dicronylic acids, poly(terephthalic hydrazide), and poly(terephthalic-chloroterephthalic hydrazide);
- 25 poly(amide-hydrazides) such as poly(teterephthaloyl 1,4 aminobenzhydrazide) and those prepared from 4-amino-benzhydrazide, oxalic dibudrazide, terephthalic dihydrazide and para-aromatic diacid chlorides; polyester such as those of the compositions include poly(oxy-trans-
- 30 1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy-1,4-phenyl-eneoxyterephthaloyl) and poly(oxy-cis-1,4-cyclohexyleneoxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy-1,4-phenyleneoxyterephthaloyl) in methylene chloride-o-cresol poly[(oxy-trans-1,4-cyclohexylene-
- 35 oxycarbonyl-trans-1,4-cyclohexylenecarbonyl-b-oxy-(2-methyl-1,4-phenylene)oxy-terephthaloyl)] in 1,1,2,2-tetrachloroethane-o-chlorophenol-phenol (60:25:15 vol/vol/vol) and poly[oxy-trans-1,4-cyclohexyleneoxycarbonyl-trans-1,4-

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cyclohexylenecarbonyl-b-oxy(2-methyl-1,3-phenylene)oxy-terephthaloyl] in o-chlorophenol; polyazomethines such as those prepared from 4,4'-diaminobenzanilide and terephthalaldehyde, methyl-1,4-phenylenediamine and terephthalaldehyde; polyisocyanides such as poly(-phenyl ethyl isoamide), and poly(n-octyl isocyanide); polyisocyanates such as poly(n-octyl isocyanates) which include poly(n-butyl isocyanate) and poly(n-hexyl isocyanate); lyotropic crystalline polymers with

10 heterocyclic unit such as poly(1,4-phenylene-2,6-benzobisthiazole)(PBT), poly(1,4-phenylene-2,6-benzobisoxazole)(PBO), poly(1,4-phenylene-1,3,4-oxadiazole), poly(1,4-phenylene-2,6-benzobisimidazole), poly[2,5(6)-benzimidazole] (AB-PBI), poly[2,6-(1,4-

15 phenylene)-4-phenylquinoline], poly[1,1'-(4,4'-biphenylene)-6,6'-bis(4-phenylquinoline)]; polyorganophosphazines such as polyphosphazene, polybisphenoxyphosphazene and poly[bis(2,2,2'-trifluoroethylene) phosphazene]; metal polymers such as

20 those derived from by condensation of trans-bis(tri-n-butylphosphine)platinum dichloride with a bisacetylene or trans-bis(tri-n-butylphosphine)bis(1,4-butadiynyl)platinum and similar combinations in the presence of cuprous iodine and an amide; cellulose and cellose derivatives such as

25 esters of cellulose which include triacetate cellulose, acetate cellulose, acetate-butyrate cellulose, nitrate, and sulfate, ethers of cellulose which include ethyl ether cellulose, hydroxymethyl ether cellulose, hydroxypropyl ether cellulose, carboxymethyl ether cellulose, ethyl

30 hydroxyethyl ether cellulose, cyanoethylethyl ether cellulose, ether-esters of cellulose such as acetoxyethyl ether cellulose and benzyloxypropyl ether cellulose, and urethane cellulose such as phenyl urethane cellulose; thermotropic liquid crystalline polymers such as

35 celluloses and their derivatives which include hydroxypropyl cellulose, ethyl cellulose propionoxypropyl cellulose; thermotropic copolyesters such as copolymers 6-hydroxy-2-naphthoic acid and p-hydroxy benzoic acid,

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copolymers of 6-hydroxy-2-naphthoic acid, terephthalic acid and hydroquinone, and copolymers of poly(ethylene-terephthalate) and p-hydroxybenzoic acid; thermotropic polymeric and thermotropic copoly(amide-ester)s.

- 5 Also illustrative of useful organic filament for use in the fabrication of backing layer 18 are those composed of extended chain polymers formed by polymerization of α,β -unsaturated monomers of the formula:



wherein:

- R_1 and R_2 are the same or different and are hydrogen, hydroxy, halogen, alkylcarbonyl, carboxy, alkoxy, alkoxy, heterocycle or alkyl or aryl either unsubstituted or substituted with one or more substituents selected from the group consisting of alkoxy, cyano, hydroxy, alkyl and aryl. Illustrative of such polymers of α,β -unsaturated monomers are polymers including
- 15 polystyrene, polyethylene, polypropylene, poly(1-octadecene), polyisobutylene, poly(1-pentene), poly(2-methylstyrene), poly(4-methylstyrene), poly(1-hexene), poly(1-pentene), poly(4-methoxystyrene), poly(5-methyl-1-hexene), poly(4-methylpentene), poly
- 25 (1-butene), polyvinyl chloride, polybutylene, polyacrylonitrile, poly(methyl pentene-1), poly(vinyl alcohol), poly(vinylacetate), poly(vinyl butyral), poly(vinyl chloride), poly(vinylidene chloride), vinyl chloride-vinyl acetate chloride copolymer, poly(vinylidene
- 30 fluoride), poly(methyl acrylate, poly(methyl methacrylate), poly(methacrylonitrile), poly(acrylamide), poly(vinyl fluoride), poly(vinyl formal), poly(3-methyl-1-butene), poly(1-pentene), poly(4-methyl-1-butene), poly(1-pentene), poly(4-
- 35 methyl-1-pentene), poly(1-hexene), poly(5-methyl-1-hexene), poly(1-octadecene), poly(vinyl-cyclopentane), poly(vinylcyclohexane), poly(α -vinyl-naphthalene), poly(vinyl methyl ether), poly(vinyl-ethylether),

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poly(vinyl propylether), poly(vinyl carbazole), poly(vinyl
pyrrolidone), poly(2-chlorostyrene), poly(4-chlorostyrene),
poly(vinyl formate), poly(vinyl butyl ether), poly(vinyl
octyl ether), poly(vinyl methyl ketone), poly(methyliso-
5 propenyl ketone), poly(4-phenylstyrene) and the like.

Illustrative of useful inorganic filament for use in
the fabrication of backing layer 18 are those glass fibers
which include quartz, magnesia aluminosilicate, non-alkaline
alumoborosilicate, soda borosilicate, soda silicate, soda
10 lime-aluminosilicate, lead silicate, non-alkaline lead
boroalumina, non-alkaline barium boroalumina, non-alkaline
zinc boroalumina, non-alkaline iron aluminosilicate,
phosphate, borate, cadmium borate, alumina fibers which
include "saffil" fiber in eta, delta, and theta phase
15 form, asbestos, boron filaments, silicone carbide fibers,
graphite and carbon fibers such as those derived from the
carbonization of polyethylene fibers, polyvinylalcohol
fibers, saras fibers, polyamide (Nomex) type fiber, nylon,
polybenzimidazole fiber, polyoxadiazole fiber,
20 polyphenylene fibers, PPR fibers, petroleum and coal
pitch (isotropic) fibers, mesophase pitch fibers,
cellulose fiber and polyacrylonitrile fiber, ceramic such
as those of the ceramic materials discussed earlier for
the use in the fabrication of ceramic Body 18 in FIG 1;
25 and metal filaments such as those formed from steel,
aluminum metal alloys and the like.

In the most preferred embodiments of the invention,
backing layer 18 is fabricated from a filament network,
which may include a high molecular weight polyethylene
30 filament, a high molecular weight polypropylene filament,
an aramid filament, a high molecular weight polyvinyl
alcohol filament, a high molecular weight poly-
acrylonitrile filament or mixtures thereof. Highly
oriented polypropylene and polyethylene filaments of
35 molecular weight at least 200,000, preferably at least one
million and more preferably at least two million may be
used in the fabrication of backing layer 18. Such high
molecular weight polyethylene and polypropylene may be

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formed into reasonably well oriented filaments by the techniques prescribed in the various references referred to above, and especially by the technique of US Patent Nos. 4,413,110, 4,457,985 and 4,663,101 and preferable US Patent Application Serial Nos. 895,396, filed August 11, 1986, and 069,684, filed July 6, 1987. Since polypropylene is a much less crystalline material than polyethylene and contains pendant methyl groups, tenacity values achievable with polypropylene are generally substantially lower than the corresponding values for polyethylene. Accordingly, a suitable tenacity is at least about 8 grams/denier, with a preferred tenacity being at least about 11 grams/denier. The tensile modulus for polypropylene is at least about 160 grams/denier, preferably at least about 200 grams/denier.

High molecular weight polyvinyl alcohol filaments having high tensile modulus preferred for use in the fabrication of backing layer 18 are described in USP 4,440,711 to Y. Kwon et al., which is hereby incorporated by reference to the extent it is not inconsistent herewith. In the case of polyvinyl alcohol (PV-OH), PV-OH filament of molecular weight of at least about 200,000. Particularly useful PV-OH filament should have a modulus of at least about 300 g/denier, a tenacity of at least about 7 g/denier (preferably at least about 10 g/denier, more preferably at about 14 g/denier, and most preferably at least about 17 g/denier), and an energy to break of at least about 8 joules/g. PV-OH filaments having a weight average molecular weight of at least about 200,000, a tenacity of at least about 10 g/denier, a modulus of at least about 300 g/denier, and an energy to break of about 8 joules/g are more useful in producing a ballistic resistant article. PV-OH filament having such properties can be produced, for example, by the process disclosed in US Patent No. 4,599,267.

In the case of polyacrylonitrile (PAN), PAN filament for use in the fabrication of layer 18 are of molecular weight of at least about 4000,000. Particularly useful

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PAN filament should have a tenacity of at least about 10 g/denier and an energy-to-break of at least about 8 joule/g. PAN filament having a molecular weight of at least about 4000,000, a tenacity of at least about 15 to
5 about 20 g/denier and an energy-to-break of at least about 8 joule/g is most useful in producing ballistics resistant articles; and such filaments are disclosed, for example, in US 4,535,027.

In the case of aramid filaments, suitable aramid
10 filaments for use in the fabrication of girdle 14 are those formed principally from aromatic polyamide are described in US Patent No. 3,671,542, which is hereby incorporated by reference. Preferred aramid filament will have a tenacity of at least about 20 g/d, a tensile
15 modulus of at least about 400 g/d and an energy-to-break at least about 8 joules/gram, and particularly preferred aramid filaments will have a tenacity of at least about 20 g/d, a modulus of at least about 480 g/d and an energy to break of at least about 20 joules/gram. Most preferred
20 aramid filaments will have a tenacity of at least about 20 g/denier, a modulus of at least about 900 g/denier and an energy-to-break of at least about 30 joules/gram. For example, poly(phenylenediamine terephthalamide) filaments produced commercially by Dupont Corporation under the
25 trade name of Kevlar[®] 29, 49, 149 and 129 are particularly useful in forming ballistic resistant composites. Also useful in the practice of this invention is poly(meta-phenylene isophthalamide) filaments produced commercially by Dupont under the trade name Nomex.

30 In the more preferred embodiments of this invention, backing layer 18 is formed of filaments arranged in a network which can have various configurations. For example, a plurality of filaments can be grouped together to form a twisted or untwisted yarn. The filaments or
35 yarn may be formed as a flat knitted or woven (plain, basket, sating and crow feet weaves, etc.) into a network, or formed into a network by any of a variety of conventional techniques. In the preferred embodiments of

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the invention, the filaments are untwisted mono-filament yarn wherein the filaments are parallel, unidirectionally aligned. For example, the filaments may also be formed into nonwoven cloth layers by convention techniques.

5 Wetting and adhesion of fiber to the polymer matrices, such as epoxy resins is enhanced by prior treatment of the surface of the yarn. The method of surface treatment may be chemical, physical or a combination of chemical and physical actions. Examples of
10 purely chemical treatments are used of SO_3 or chlorosulfonic acid. Examples of combined chemical and physical treatments are corona discharge treatment or plasma treatment using one of several commonly available machines.

15 In the most preferred embodiments of this invention, backing layer 18 is composed by one or more layers of continuous fibers embedded in a continuous phase of matrix material which preferably substantially coats each
20 filament contained in the bundle of filaments. The manner in which the filaments are dispersed may vary widely. The filaments may be aligned in a substantially parallel, unidirectional fashion, or filaments may be aligned in a multidirectional fashion, or filaments may be aligned in a
25 multidirectional fashion with filaments at varying angles with each other. In preferred embodiments of this invention, filaments in each layer forming backing layer 18 are aligned in a substantially parallel, unidirectional fashion such as in a prepreg, pultruded sheet and the like.

The matrix material used in the formation of backing
30 layer 18 may vary widely. Illustrative of use for matrix materials are thermoplastic polymers such as polyesters, polyamides, polyurethanes, polyolefins, polycarbonates, polyamides, polyphenyloxides, polyurethane elastomers, polyesteramides, polylactones, polyester carbonates,
35 polyphenylene sulfides and the like; and thermosetting resins such as epoxy resins, phenolic resins, vinyl ester resins, modified phenolic resins, unsaturated polyester, allylic resins, alkyd resins, urethanes and melamine urea

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resins and the like. A single material may be used as the matrix or blends can be used. In the preferred embodiments of the invention, the matrix material is a mixture of a thermoplastic resins and a thermosetting resin. The preferred thermosetting material is a vinyl ester resin and the preferred thermoplastic resin is a polyurethane.

The proportions of matrix to filament in backing layer 18 is not critical and may vary widely depending on a number of factors including, whether the matrix material has any ballistic-resistant properties of its own (which is generally not the case) and upon the rigidity, shape, heat resistance, wear resistance, flammability resistance and other properties desired for backing layer 18. In general, the proportion of matrix to filament in backing layer 18 may vary from relatively small amounts where the amount of matrix is about 10% by volume of the filaments to relatively large amount where the amount of matrix is up to about 90% by volume of the filaments. In the preferred embodiments of this invention, matrix amounts of from about 15 to about 80% by volume are employed. All volume percents are based on the total volume of backing layer 18. In the particularly preferred embodiments of the invention, ballistic-resistant articles of the present invention, layer 18 contains a relatively minor proportion of the matrix (e.g., about 10 to about 30% by volume of composite), since the ballistic-resistant properties are almost entirely attributable to the filaments, and in the particularly preferred embodiments of the invention, the proportion of the matrix in backing layer 18 is from about 10 to about 30% by weight of filaments.

Backing layer 18 can be fabricated using conventional procedures. For example, in those embodiments of the invention where backing layer 18 is a metal, alloy or an alloy or metal containing inorganic fibrous reinforced layer 18 can be formed by conventional metal working techniques. In the most preferred embodiments of the invention in which backing layer 18 is a woven fabric

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composed of a polymeric material, backing layer 18 can be fabricated using conventional fabric weaving techniques of the type commonly employed for ballistic purposes such as a plain weave or a Panama weave. In those preferred

5 embodiments of the invention in which backing layer 18 is a network of polymeric fibers in a matrix, backing layer 18 is formed by molding the combination of fibers and matrix material in the desired configurations and amounts, and then subjecting the combination to heat and pressure.

10 For extended chain polyethylene filaments used in the most preferred embodiments, molding temperatures range from about 20 to about 150°C, preferably from about 80 to about 145°C, more preferably from about 100 to about 135°C, and more preferably from about 110 to about 130°C. The
15 pressure may range from about 10 psi (69 kpa to about 10,000 psi (69,000 kpa). A pressure between about 10 psi (69 kpa) and about 100 psi (690 kpa), when combined with temperatures below about 100 C for a period of time less than about 1.0 min., may be used simply to cause adjacent
20 filaments to stick together. Pressures from about 100 psi to about 10,000 psi (69,000 kpa), when coupled with temperatures in the range of about 100 to about 155°C for a time of between about 1 to about 5 min., may cause the filaments to deform and to compress together (generally in
25 a film-like shape). Pressures from about 100 psi (690 kpa) to about 10,000 psi (69,000 kpa), when coupled with temperatures in the range of about 150 to about 155°C for a time of between 1 to about 5 mn., may cause the film to become translucent or transparent. For polypropylene
30 filaments, the upper limitation of the temperature range would be about 10 to about 20°C higher than for ECPE filament.

 In the most preferred embodiments of the invention, the polymeric filaments (pre-molded if desired) are
35 pre-coated with the desired matrix material prior to being arranged in a network and molded into backing layer 18 as described above. The coating may be applied to the filaments in a variety of ways and any method known to

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those of skill in the art for coating filaments may be used. For example, one method is to apply the matrix material to the stretched high modulus filaments either as a liquid, a sticky solid or particles in suspension, or as
5 fluidized bed. Alternatively, the matrix material may be applied as a solution or emulsion in a suitable solvent which does not adversely affect the properties of the filament at the temperature of application. In these illustrative embodiments, any liquid may be used.

10 However, in the preferred embodiments of the invention in which the matrix material is an elastomeric material, preferred groups of solvents include water, paraffin oils, ketones, alcohols, aromatic solvents or hydrocarbon solvents or mixtures thereof, with illustrative specific
15 solvents including paraffin oil, xylene, toluene and octane. The techniques used to dissolve or disperse the matrix in the solvents will be those conventionally used for the coating of similar elastomeric materials on a variety of substrates. Other techniques for applying the
20 coating to the filaments may be used, including coating of the high modulus precursor (gel filament) before the high temperature stretching operation, either before or after removal of the solvent from the filament. The filament may then be stretched at elevated temperatures to produce
25 the coated filaments. The gel filament may be passed through a solution of the appropriate matrix material, as for example an elastomeric material dissolved in paraffin oil, or an aromatic or aliphatic solvent, under conditions to attain the desired coating. Crystallization of the
30 polymer in the gel filament may or may not have taken place before the filament passes into the cooling solution. Alternatively, the filament may be extruded into a fluidized bed of the appropriate matrix material in powder form.

35 The proportion of coating on the coated filaments or fabrics in backing layer 18 may vary from relatively small amounts of (e.g. 1% by weight of filaments) to relatively large amounts (e.g. 150% by weight of filaments),

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depending upon whether the coating material has any impact or ballistic-resistant properties of its own (which is generally not the case) and upon the rigidity, shape, heat resistance, wear resistance, flammability resistance and other properties desired for the complex composite article. In general, backing layer 18 containing coated filaments should have a relatively minor proportion of coating (e.g. about 10 to about 30 percent by volume of filaments), since the ballistic-resistant properties of girdle 14 are almost entirely attributable to the filament. Nevertheless, coated filaments with higher coating contents may be employed. Generally, however, when the coating constitutes greater than about 60% (by volume of filament), the coated filament is consolidated with similar coated filaments to form a fiber layer without the use of additional matrix material.

Furthermore, if the filament achieves its final properties only after a stretching operation or other manipulative process, e.g. solvent exchanging, drying or the like, it is contemplated that the coating may be applied to a precursor material of the final filament. IN such cases, the desired and preferred tenacity, modulus and other properties of the filament should be judged by continuing the manipulative process on the filament precursor in a manner corresponding to that employed on the coated filament precursor. Thus, for example, if the coating is applied to the xerogel filament described in US Application Serial No. 572,607 of Kavesh et al., and the coated xerogel filament is then stretched under defined temperature and stretch ratio conditions, then the filament tenacity and filament modulus values would be measured on uncoated xerogel filament which is similarly stretched.

It is a most preferred aspect of the invention that each filament be substantially coated with the matrix material for the production of backing layer 18. A filament is substantially coated by using any of the coating processes described above or can be substantially

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coated by employing any other process capable of producing a filament coated essentially to the same degree as a filament coated by the processes described heretofore (e.g., by employing known high pressure molding

5 techniques).

The filaments and networks produced therefrom are formed into "simple composites" as the precursor to preparing a more complex backing layer 18. The term, "simple composite", as used herein is intended to mean
10 composites made up of one or more layers, each of the layers containing filaments as described above with a single major matrix material, which material may include minor proportions of other materials such as fillers, lubricants or the like as noted heretofore.

15 The proportion of matrix material to filament is variable for the simple composites, with matrix material amounts of from about 5% to about 150 vol %, by volume of the filament, representing the broad general range. Within this range, it is preferred to use composites
20 having a relatively high filament content, such as composites having only about 10 to about 50 vol % matrix material, by volume of the composite, and more preferably from about 10 to about 30 vol % matrix material by volume of the composite.

25 Stated another way, the filament network occupies different proportions of the total volume of the simple composite. Preferably, however, the filament network comprises at least about 30 volume percent of the simple composite. For ballistic protecting, the filament network
30 comprises at least about 50 volume percent, more preferably about 70 volume percent, and most preferably at least about 75 volume percent, with the matrix occupying the remaining volume.

A particularly effective technique for preparing a
35 preferred composite of this invention comprised of substantially parallel, undirectionally aligned filaments includes the steps of pulling a filament or bundles of filaments through a bath containing a solution of a matrix

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material preferably, an matrix material, and circumferentially winding this filament into a single sheet-like layer around and along a bundle of filaments the length of a suitable form, such as a cylinder. The solvent is then evaporated leaving a sheet-like layer of filaments embedded in a matrix that can be removed from the cylindrical form. Alternatively, a plurality of filaments or bundles of filaments can be simultaneously pulled through the bath containing a solution or dispersion of a matrix material and laid down in closely positioned, substantially parallel relation to one another on a suitable surface. Evaporation of the solvent leaves a sheet-like layer comprised of filaments which are coated with the matrix material and which are substantially parallel and aligned along a common filament direction. The sheet is suitable for subsequent processing such as laminating to another sheet to form composites containing more than one layer.

Similarly, a yarn-type simple composite can be produced by pulling a group of filament bundles through a dispersion or solution of the matrix material to substantially coat each of the individual filaments, and then evaporating the solvent to form the coated yarn. The yarn can then, for example, be employed to form fabrics, which in turn, can be used to form more complex composite structures. Moreover, the coated yarn can also be processed into a simple composite by employing conventional filament winding techniques; for example, the simple composite can have coated yarn formed into overlapping filament layers.

The number of layers of fibers included in backing layer 18 may vary widely. In general, the greater the number of layers the greater the degree of ballistic protection provided and conversely, the lesser the number of layers the lesser the degree of ballistic protection provided.

One preferred configuration of backing layer 18 is a laminate in which one or more layers of filaments coated

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with matrix material (pre-molded if desired) are arranged in a sheet-like array and aligned parallel to one another along a common filament direction. Successive layers of such coated unidirectional filaments can be rotated with respect to the previous layer after which the laminate can be molded under heat and pressure to form the laminate. An example of such a layered vibration isolating layer is the layered structure in which the second, third, fourth and fifth layer are rotated 45° , 45° , 90° and 0° with respect to the first layer, but not necessarily in that order. Similarly, another example of such a layered layer 12 is a layered structure in which the various unidirectional layers forming girdle are aligned such that the common filament axis is adjacent layers is 0° , 90° .

FIG 2 shows a variant of the embodiment of FIG 1 which is indicated at 22. In composite 22, the ceramic impact layer 10 is covered with cover layer 24 which functions as an anti-spall layer to retain spall or particles resulting from the shattering of ceramic bodies 20 by a striking projectile and to maintain ceramic bodies 20 in position. In FIG 2, cover layer 24 consists of top cover 26 and release layer 28. Top cover 26 is formed from a rigid material, as for example, the materials useful in the construction of backing layer 18.

Illustrative of such materials are metals such as steel, titanium and aluminum alloys, or of a rigid high strength polymeric composite such as a thermoplastic resin such as a polyurethane, a polyester or a polyamide, a thermosetting resin such as epoxy, phenolic or vinyl ester resin reinforced with polymeric filaments such as aramid or extended chain polyethylene or inorganic filaments such as S-glass fibers, silicon carbide fibers, E-glass fibers, carbon fibers, boron fibers and the like. Release layer 28 is formed from materials used in the fabrication of backing layer 34 which are fibrous composites comprised of a fiber network which optionally may be in a matrix in a matrix. Release layer 32 functions to eliminate or to substantially reduce the strain on unhit ceramic bodies 20

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in the deformation of the composites from impact by the projectile. The construction of ceramic impact layer 12, peripheral hard impact layer retaining means 14 and peripheral ceramic body retaining means 16, and their materials of construction are the same as in article 10 of FIG 1.

FIG 3 depicts an armor plate composite 30 which differs from the armor plate 22 of FIG 2 by the inclusion of a vibration isolating layer 32, corresponding parts being referred to by like numerals. Vibration isolating layer 32 minimizes the shock and vibration resulting from the impact of the projectiles which inhibits the transmission of shock and vibration to portions of ceramic impact layer 12 away from the point of impact which substantially increases the multiple hit capability of the armor. In armor plate 30, vibration isolating layer 32 is composed of three superimposed constituent, essential layer 34 and two optional layers 36 and 38. Optional layers 34 and 38 are thin layers of a metal or non-metal rigid material such as the materials used in the fabrication of backing layer 18 and layer 34 is one or more layers comprising a network of polymeric fibers (such as the extended chain polyethylene fibers) used in the fabrication of backing layer 18, which may be optionally and preferably in a matrix. Rigid layers 42 and 44 function to improve the overall performance of vibration isolation layer 32, to improve the surface characteristics of vibration isolation layer 32, to provide a surface on which ceramic bodies 20 can be attached; and to retain dimensional stability (i.e. flatness and straightness) of the surface subject severe impact deformation. At their contact points, constituent layer 34, 36 and 38 are bonded together with a suitable agent such as an adhesive as for example, the flexible adhesives described above for use to bond ceramic bodies 20 to backing layer 18 such as a polysulfide or an epoxy. In composite 30, backing layer 18 is of double layer construction and includes rigid layer 40 which is formed of a metal or rigid polymeric

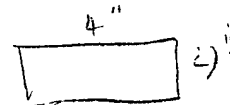
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material such as glass filled epoxy resin and ballistic resistant composite layer 42 and preferably formed from high strength fibers such as Spectra[®] polyethylene fibers or aramid fibers in a polymeric matrix. The construction of cover layer 30, ceramic impact layer 12, peripheral hard impact layer retaining means 14 and peripheral ceramic body retaining means 16 and their materials of construction are the same as in composite 10 of FIG 1.

Complex ballistic articles of this invention have many uses. For example, such composites may be incorporated into more complex composites to provide a rigid complex composite article suitable, for example; as structural ballistic-resistant components, such as helmets, structural members of aircraft, and vehicle panels.

The following examples are presented to provide a more complete understanding of the invention. The specific techniques, condition, materials, proportions and reported data set forth to illustrate the principles of the invention are exemplary and should not be construed as limiting the scope of the invention.

EXAMPLE I



1.5 cm x 1.5 cm

A panel consisting of a 4 by 4 checker board with square cell of dimensions of 4" (10.2 cm) by 4" (10.2 cm) by 1/2" (1.3 cm) depth was constructed. The cells of the panel were divided with a 0.06" (0.15 cm) thick aluminum barrier wall. Each cell was filled with one alumina tile. The panel was constructed with Spectra[®] composite as backing material to prevent damages of the tiles from shocks and vibrations induced by the ammunition hits. The checker board was placed into a 16.25" (41.3 cm) by 16.25" (41.3 cm) by 1/2" (1.3 cm) aluminum frame, and it was covered with a piece of 1/8" (0.319 cm) thick aluminum. A piece of Spectra[®] fabric which was used as a release material was placed in between the surface of the segmented layer of tiles and the cover. The style of the

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fabric used was 952 plain 650d. The whole unit was mounted on a rigid, 21/32" (1.67 cm) thick, glass reinforced plastic (GRP) plate. The adhesive used was sold by Semco/Bancroft Corp. of New Jersey under a trade name of P/S 890-B 1/2 for the adhesive and the trade name for the curing agent was PR-890-B 1/2. The composition used was 10 to 1 ratio between the adhesive and the curing agent. The cure time required was around 12 hours, and the tack free time was about 2 hours. This adhesive meets the MIL-S-8802E specs.

EXAMPLE II

The multiple-hit capability of the article of EXAMPLE I was evaluated. In these experiments, the tiles were shot by a projectile traveling at a speed around 3100 ft/sec.(945 m/sec). After 12 hits, the remaining four (4) unhit tiles remained undamaged. The location and distribution of cracks were confined in the panel composed of brittle solids at the point of impact. The cracks and flaws initiated around the indentation were localized only at the point of contact loading for the tile which was hit and did not propagate in the entire panel. Spalls/particles created by the shattering of tile upon impact are retained locally around the point of impact. Visual inspection of neighboring tiles found that they were not damaged by spalls/particles created by comminution of the tiles on impact.

EXAMPLE III

Example II was repeated with the exception that marble tiles were used and the flexible bonding agent was replaced by inflexible vinyl ester resin. One Thousand grams of a mixture of a vinyl ester resin (VE 8520 sold by Interplastics) and peroxide (Benzoate peroxide sold by Lucidol under the trade name Luperco AFR-400) and a promoter (N, N, dimetyl anilane) was poured in the mold

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until the article was completely covered. The composition of the vinyl ester resin/peroxide/promotor is 10/0.1/0.006. The material was cured for two hours at room temperature under pressure. The article was evaluated as in EXAMPLE 5 II, and it exhibited multiple hit capability.

EXAMPLE IV

A panel was constructed as described in Example II 10 with the exception that no Spectra® composite vibration and shock isolation material was used. The panel was tested following the conditions described in Example II. While the panel exhibited multiple hit capability at was not as effective as the panel of Example I. Cracks were found 15 around the neighboring unhit tiles after the impact. Therefore, the performance at the center of tile and at the seam area of the segmented for another hit was not as good as in the panel of Example I.

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EXAMPLE V

A panel was constructed following the procedure described in Example II with the exception that no elastic barrier wall was used. The panel was tested following the 25 conditions described in Example II. While the panel exhibited multiple hit capability, it was not as effective as the panel of Example I. Cracks were found around the neighboring unhit tiles after the impact. Therefore, the performance at the center of tile and at the seams between 30 adjacent tiles for another hit was not as good as in the panel of Example I.

EXAMPLE VI

35 A panel was constructed following the procedure described in Example I with the exception that a rigid bonding agent (thermosetting polyester resin) was used to bond the ceramic bodies to the backing layer. The panel

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was tested following the conditions described in Example I. While the panel exhibited multiple hit capability, it was not as effective as the panel of Example I. Cracks were found around the neighboring unhit tiles after the impact. Also, some of the neighboring tiles were delaminated from the substrata. Therefore, the performance at the center of tile and at the seams between adjacent tiles for another hit was not as good as in the panel of Example I.

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EXAMPLE VII

A panel was constructed following the procedure described in Example I with the exception that no release material was used. The panel was tested following the conditions described in Example II. While the panel exhibited multiple hit capability, it was not as effective as the panel of Example I. Cracks were found around the neighboring unhit tiles after the impact.

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EXAMPLE VIII

The efficiency of the penetration resistance of Example I was evaluated at the center of tile, seam, edge, and corner, following the experimental procedure described in Example II. It was found that, compared to the center of tile, the efficiency was at least 99% for the seam, edge, and corner.

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COMPARATIVE EXAMPLE I

A panel was constructed following the procedure described in Example I with the exception that no peripheral frame was used to surround the edges of the segmented layer of tiles. The panel was tested following the conditions described in Examples II. The performance of the edges reduced drastically, down to about 20% of the performance at the center of the tiles. Cracks were found

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around the neighboring unhit tiles after the impact. Also, some of the neighboring tiles were delaminated from the substrata. Therefore, the performance at the neighboring areas of the hit for another hit was poor, and
5 the panel did not exhibit acceptable multiple hit capability.

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WHAT IS CLAIMED IS:

1. A multilayer complex armore comprising:
 - (a) hard impact layer comprised of one or more ceramic bodies bonded to a surface of a backing layer;
 - 5 (b) peripheral hard impact layer retaining means positioned about the outer periphery of said hard impact layer and in contact therewith; and
 - (c) peripheral ceramic body retaining means comprising an interconnected network positioned about
10 the periphery of each of said ceramic bodies comprising said hard impact layer.
2. The armor of claim 1 which further comprises a cover layer and a release layer, said release layer in
15 comprises a cover layer and a release layer, said release layer in contact with and attached to a side of the hard impact layer; and
said cover layer on the side opposite the side thereof
3. The armor of claim 2 which further comprises a
20 vibration isolating layer positioned between and attached to said hard impact layer and said backing layer,
said vibration isolating layer comprising a network of high strength polymer filaments having a
25 tenacity of at least about 7 grams.denier, a tensile modulus of at least about 160 grams/denier and an energy-to-break of at least about 8 joules/gram.
4. The armor of claim 1 wherein said peripheral ceramic body retaining means comprises a plurality of
30 substantially flat elongated bodies positioned between adjacent rows of ceramic bodies, a plurality of said bodies intersecting at an angle and interlocking at the point of intersection.
5. The armor of claim 1 wherein the % efficiency
35 of peretration resistance at or about the seams of adjacent ceramic bodies, at about the edge of said ceramic bodies and at or about the corner of said

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ceramic bodies is at least about 60% of the % efficiency at or about the center of said ceramic bodies.

6. The armor of claim 1 wherein the % efficiency
5 of penetration resistance at or about the seams
between adjacent ceramic bodies is at least about 80%
of the % efficiency at or about the center of at least
one of said ceramic bodies, the % efficiency at or
about an edge of ceramic bodies is at least about 70%
10 of the % efficiency at or about the center of at least
one ceramic body 20 is at least about 60% of the %
efficiency at or about the center of at least one
ceramic body.

7. The armor of claim 6 wherein the % efficiency
15 at or about the seams between adjacent ceramic bodies,
at or about an edge of each ceramic body and at or
about a corner of each ceramic body is at least about
95% of the % efficiency at or about the center of each
ceramic body.

8. The armor of claim 7 wherein the % efficiency
20 at or about the seams between adjacent ceramic bodies,
at or about an edge of each ceramic body and at or
about a corner of each ceramic body is at least about
99% of the % efficiency at or about the center of each
25 ceramic body.

9. The armor of claim 1 wherein said ceramic
impact layer comprises a plurality of ceramic bodies.

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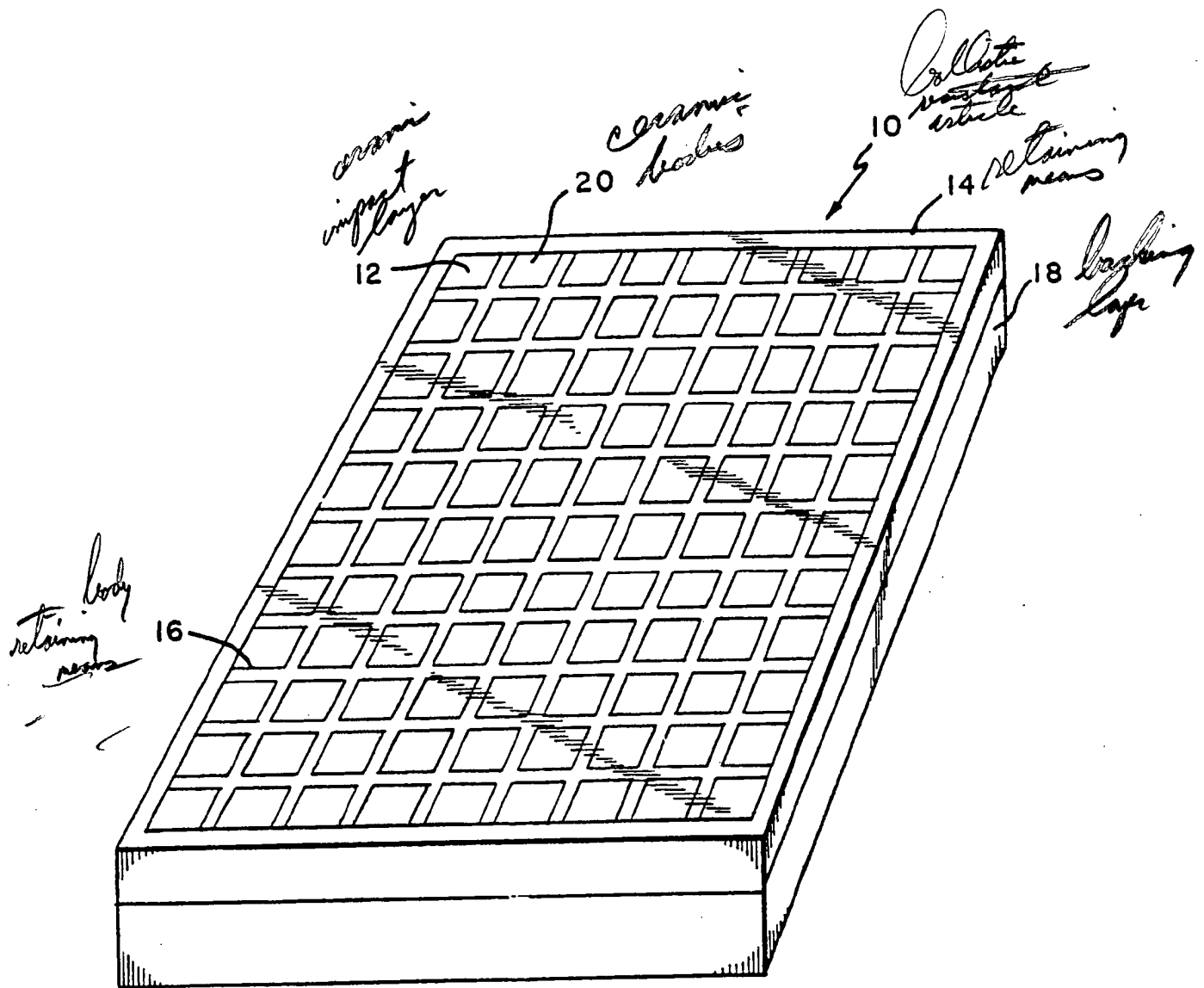


FIG. 1

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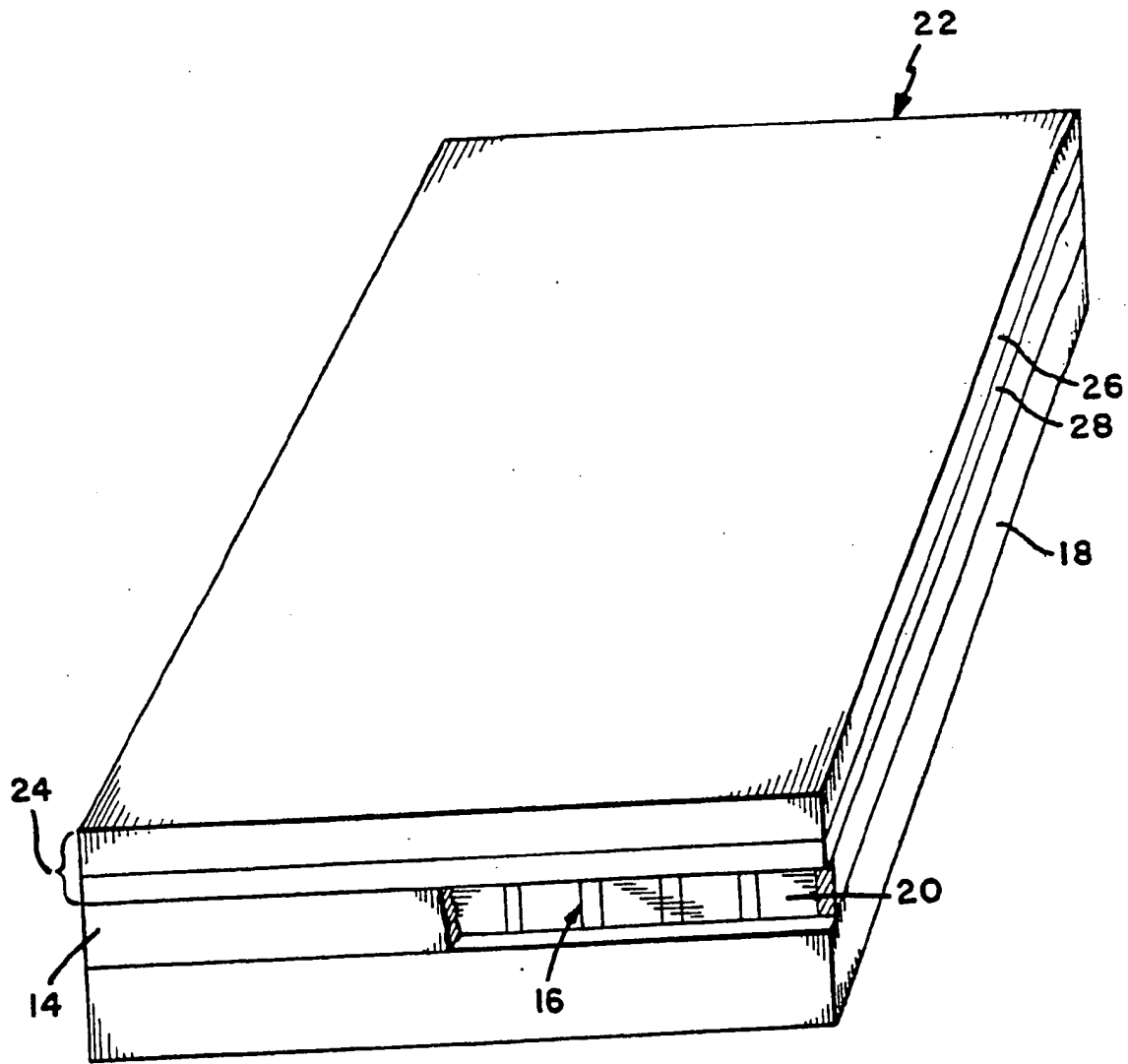


FIG. 2

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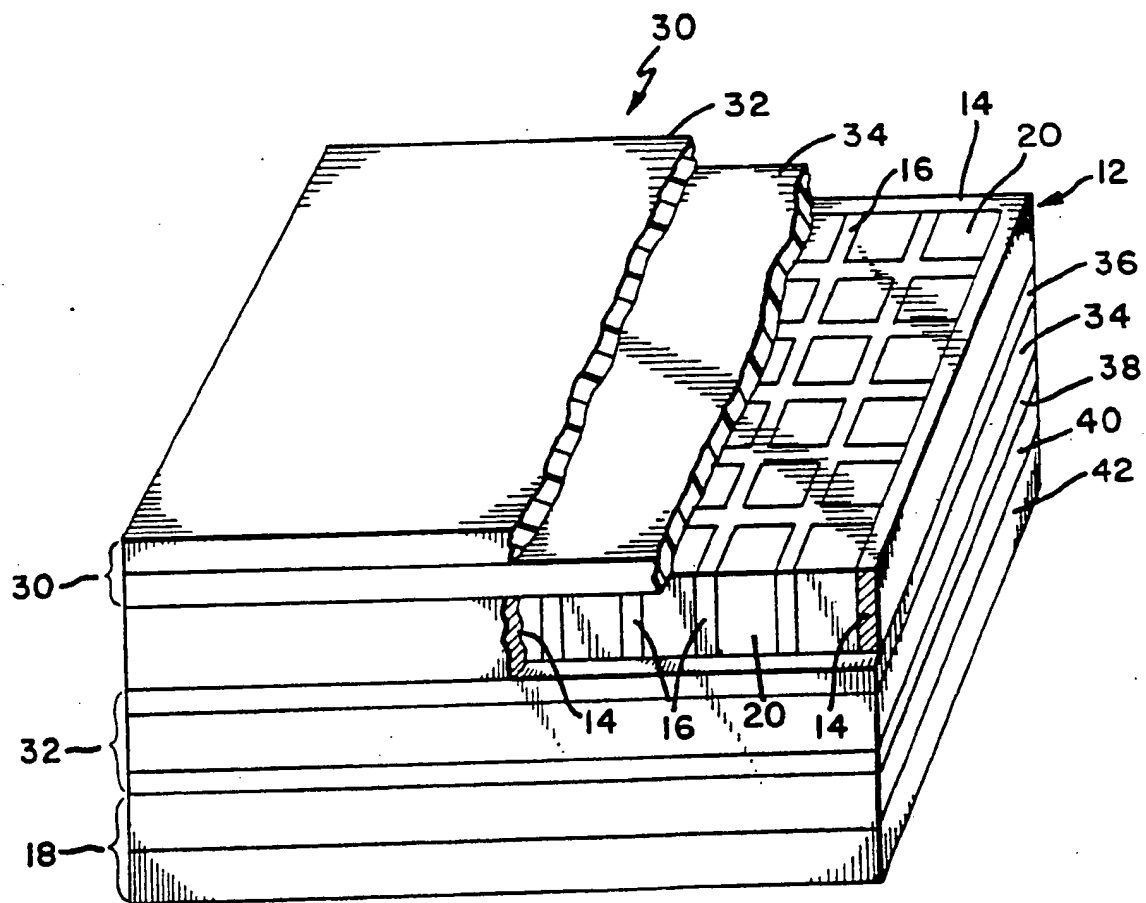


FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/06453

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: F 41 H 5/04, B 32 B 18/00, B 32 B 5/16																	
II. FIELDS SEARCHED <div style="text-align: right; font-size: small;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 20%; border: none;">Classification System</td> <td style="border: none;">Classification Symbols</td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;">IPC5</td> <td style="border: 1px solid black; padding: 5px;">B 32 B; F 41 H</td> </tr> </table> <div style="text-align: center; font-size: x-small;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸</div>			Classification System	Classification Symbols	IPC5	B 32 B; F 41 H											
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III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; font-size: x-small;">Category[*]</th> <th style="width: 70%; font-size: x-small;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 20%; font-size: x-small;">Relevant to Claim No.¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>US, A, 3616115 (N. KLIMMEK) 26 October 1971, see the whole document <div style="text-align: center;">--</div></td> <td style="text-align: center; vertical-align: top;">1,2,4,9</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>GB, A, 2149482 (H. APPRICH) 12 June 1985, see figure 7 <div style="text-align: center;">--</div></td> <td style="text-align: center; vertical-align: top;">1,3,9</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>EP, A1, 0041271 (GORUM, A.E.) 9 December 1981, see figure land6 <div style="text-align: center;">--</div></td> <td style="text-align: center; vertical-align: top;">1,9</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>EP, A1, 0312399 (LASAR S.P.A.) 19 April 1989, see the whole document <div style="text-align: center;">--</div></td> <td style="text-align: center; vertical-align: top;">1,9</td> </tr> </tbody> </table> <div style="font-size: x-small; margin-top: 10px;"> <div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>[*] Special categories of cited documents: ¹⁰</p> <p>^{"A"} document defining the general state of the art which is not considered to be of particular relevance</p> <p>^{"E"} earlier document but published on or after the international filing date</p> <p>^{"L"} document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>^{"O"} document referring to an oral disclosure, use, exhibition or other means</p> <p>^{"P"} document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>^{"T"} later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>^{"X"} document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>^{"Y"} document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>^{"&"} document member of the same patent family</p> </div> </div> </div>			Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	US, A, 3616115 (N. KLIMMEK) 26 October 1971, see the whole document <div style="text-align: center;">--</div>	1,2,4,9	X	GB, A, 2149482 (H. APPRICH) 12 June 1985, see figure 7 <div style="text-align: center;">--</div>	1,3,9	X	EP, A1, 0041271 (GORUM, A.E.) 9 December 1981, see figure land6 <div style="text-align: center;">--</div>	1,9	X	EP, A1, 0312399 (LASAR S.P.A.) 19 April 1989, see the whole document <div style="text-align: center;">--</div>	1,9
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IV. CERTIFICATION <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> <div style="border: 1px solid black; padding: 5px; margin-bottom: 5px;"> Date of the Actual Completion of the International Search 13th February 1991 </div> <div style="border: 1px solid black; padding: 5px;"> International Searching Authority EUROPEAN PATENT OFFICE </div> </td> <td style="width: 50%; border: none; vertical-align: top;"> <div style="border: 1px solid black; padding: 5px; margin-bottom: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center; font-weight: bold; font-size: 1.2em;">07 MAR 1991</div> </div> <div style="border: 1px solid black; padding: 5px;"> Signature of Authorized Officer <div style="text-align: center;"> MISS T. TAZELAAR </div> </div> </td> </tr> </table>			<div style="border: 1px solid black; padding: 5px; margin-bottom: 5px;"> Date of the Actual Completion of the International Search 13th February 1991 </div> <div style="border: 1px solid black; padding: 5px;"> International Searching Authority EUROPEAN PATENT OFFICE </div>	<div style="border: 1px solid black; padding: 5px; margin-bottom: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center; font-weight: bold; font-size: 1.2em;">07 MAR 1991</div> </div> <div style="border: 1px solid black; padding: 5px;"> Signature of Authorized Officer <div style="text-align: center;"> MISS T. TAZELAAR </div> </div>													
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 3431818 (H.A. KING) 11 March 1969, see the whole document --	1-9
A	US, A, 3444033 (H.A. KING) 13 May 1969, see the whole document --	1-9
A	WO, A1, 8303895 (PEQUIGNOT, M.) 10 November 1983, see the whole document --	1-9
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P	US, A, 4911061 (PIVITT ET AL) 27 March 1990, see the whole document -- -----	1-9

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/US 90/06453

SA 42411

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 28/12/90
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3616115	26/10/71	NONE	
GB-A- 2149482	12/06/85	DE-A- 3228264 FR-A-B- 2573193	05/12/85 16/05/86
EP-A1- 0041271	09/12/81	AU-D- 7088581	10/12/81
EP-A1- 0312399	19/04/89	NONE	
US-A- 3431818	11/03/69	DE-A- 1578324	02/01/70
US-A- 3444033	13/05/69	NONE	
WO-A1- 8303895	10/11/83	DE-T- 3342776 FR-A- 2526535	17/05/84 10/11/83
FR-A1- 2632059	01/12/89	NONE	
FR-A1- 2637063	30/03/90	NONE	
US-A- 4911061	27/03/90	DE-A- 4008741	27/09/90

For more details about this annex : see Official Journal of the European patent Office, No. 12/82